On the Boiling Point of Water.

By The Earl of Berkeley, F.R.S., and M. P. Appleby, M.A., B.Sc. (Oxon).

(Received March 23, 1911.)

Introduction.—In the course of some work, communicated to the Royal Society* by one of us, in which determinations of the boiling points of some saturated solutions were made by Buchanan's method (the so-called Landsberger-Sakurai method), it was pointed out that these boiling points probably varied according to the height of liquid operated upon. During the course of that research a few experiments, which, however, are not recorded in the paper, were made on the boiling point of water; and it was found that this boiling point was approximately that due to a head of water equal to half the total height of liquid.

The paper cited mentioned the hope that direct osmotic pressure measurements might be obtained; this hope has not been fulfilled, but as an exact connection between the vapour-pressure and the osmotic pressure of a solution has since been worked out,† a knowledge of the boiling points will enable the osmotic pressure to be calculated.

In the same paper it was pointed out that more accurate results might be obtained by means of platinum thermometers, and as a preliminary it was thought advisable to investigate, if possible, the relation between the pure solvent's boiling point and the conditions under which it is being observed.

Apparatus and Method of Determination.—Fig. 1 gives a diagrammatic representation of the electric connections, together with a section through the apparatus in which the boiling points were determined. This vessel, which is shown at A, is thoroughly lagged; water is boiled in the lower part and its vapour is forced through B and through the water in C (the boiling-point vessel proper), to be condensed at D, and the amount condensed measured in the graduated cylinder E. C is graduated, along its vertical axis, in centimetres and half centimetres, and is closed by an india-rubber stopper, through which is passed one of the platinum thermometers T_1. The other thermometer T_2 is placed in the hypsometer F.

The two thermometers were obtained from the Cambridge Scientific Instrument Company, and were placed, as shown, at the ends of the Wheatstone bridge wire. They were furnished with compensating leads, but these are omitted from the diagram. Each thermometer had a resistance of about 7 ohms at 100° C., and a fundamental interval of 2 ohms.

---

* Berkeley, 'Phil. Trans.,' 1904, A, vol. 203.

† Porter, 'Roy. Soc. Proc.,' 1907, A, vol. 79, p. 521.

The bridge,* also made by the Cambridge Instrument Company, was 150 mm. long, and was furnished with a sliding contact moved by a screw with a micrometer head. The position of the contact could be read to 0·01 mm., and, if necessary, estimated to 0·001 mm. The battery and galvanometer circuits were closed by means of a Griffiths reversing key so as to eliminate some of the thermo-currents.

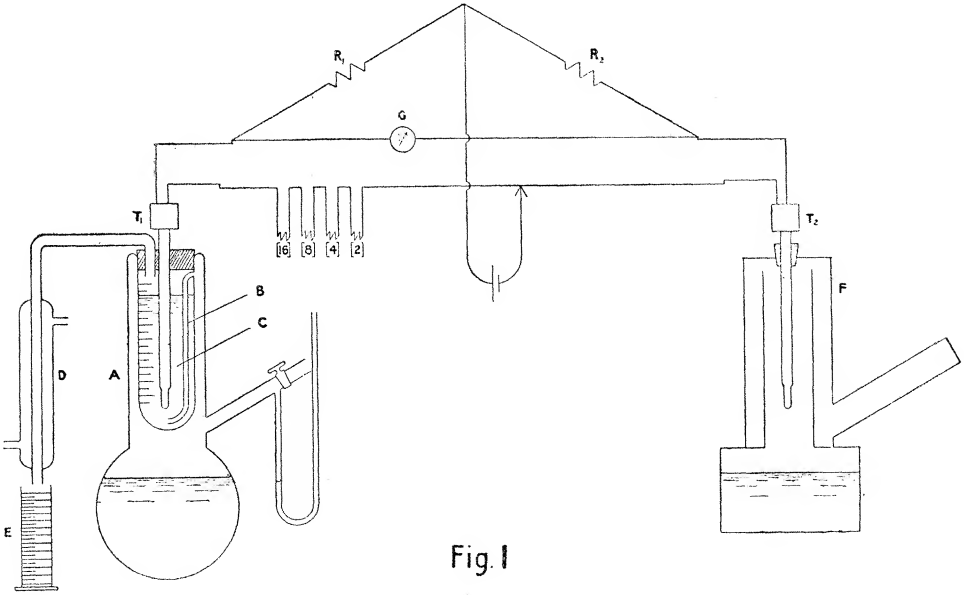


Fig. 1

The bridge wire was very carefully calibrated by the late Mr. A. E. Green, but before using it for this research it was again calibrated by Mr. J. Stephenson.

[2], [4], [8], and [16] were bridge extensions made of manganin, any one of which could be thrown in when the difference of temperature between the two thermometers was larger than could be dealt with on the bridge wire alone; they were only used in the observations on solutions. These extensions were made by Mr. Stephenson and calibrated in terms of the resistance of the mean bridge wire millimetre with the following results:—

---

* This bridge was designed for another research and is not very suitable for the work here recorded.

Table I.

Extension.	Resistance in M.B.M.		
[2]	302·84	302·12	302·06
[4]	600·59	600·47	600·49
[8]	1194·77	1194·79	1194·71
[16]	2378·37	2378·47	2378·47

R_1 and R_2 were two coils of very nearly equal resistance of 5 ohms, kindly lent to us by Principal E. H. Griffiths.

The mean resistance of 1 mm. of the bridge wire was 0·000144495 ohm. A movement of 1 mm. in the position of the sliding contact was equivalent to a temperature difference of 0·01445° C.; thus the error in reading the temperature difference between the two thermometers is not more than 0·0001° C.

Determination of the Fixed Points of the Thermometers.—The difference of resistance of the thermometers was found by finding the centre of resistance of the system—thermometer T_1, bridge extensions, bridge proper, thermometer T_2. The fixed points were determined several times by measuring—

(1) The balance-point when both thermometers were in the same hypsometer.

(2) The balance-point when one thermometer was in the hypsometer and the other in ice. For this purpose two standard 1 ohm manganin coils were connected in series with the ice thermometer, the coils being immersed in a stirred oil bath kept at 15° to 16° C.

The results of the observations under the heading (1) are given in Table II:—

Table II.—Hypsometer Point.

Date.	Bridge readings.
1910.	
January 13	84·48
April 18	84·06
May 26	84·06
July 22	83·75
October 3	84·10
" 28	84·30
November 16	84·25

It will be seen that there are slight variations in the hypsometer point, these variations are in the thermometers themselves,* for the centre of the bridge was also tested at intervals and was found not to move by more than 0·07 mm.

---

* Towards the end of the experiments it was discovered that the thermometers gave the same balance-point if the exposed part of their stems were carefully lagged and if they

The results under heading (2), which gives the fundamental interval, are recorded in Table III:—

Table III.—Fundamental Interval.

Date.	Fundamental interval.	Number of observations.
1910.	ohms.	
January 18...........	1·99985	6
April 18...........	2·00041	1
July 24...........	1·99942	4
October 4...........	1·99993	1

The Boiling Point of Water.—Two advantages accrue through the use of differential platinum thermometers. The compensating leads greatly reduce "emergent column" errors, and by having one of the thermometers always in a hypsometer, the effect of barometer changes on the boiling point of the pure liquid is automatically eliminated.

It was found early in the course of the research that the boiling point was affected not only by the height of water through which the steam had to pass, but also by the rate at which it was passing; and this obtained although the stirring was so thorough that on moving the thermometer to different positions the maximum variation was not more than 0·001° C.

The following table gives the observations on the variation in the boiling point of water:—

Column (1) gives the rate of passage of steam; that is, the number of cubic centimetres of water condensed into E (fig. 1) in 10 minutes.

Column (2) gives the height of water above the orifice of the jet B. This height is tabulated, instead of the total height of the water, for a reason which will be apparent later. The orifice was 5 mm. above the bottom of the vessel C.

Column (3) gives the "observed" difference in temperature between the two thermometers. In the experiments the actual rate of passage of steam was seldom exactly that given in (1). The numbers here tabulated are the observed differences of temperature corrected to the rates in column (1) by means of a factor which was experimentally determined.

were passed through the hypsometer cover to the same depth. Fortunately the hypsometer point was determined before each series of boiling-point observations, and during that series thermometer T_2 was never moved from its position, while T_1 was lagged, so that no error greater than other experimental errors will occur through referring each series to the previous hypsometer-point determination.

Column (4) gives the difference in temperature calculated from the assumption that the rise is directly proportional to a pressure equivalent to half the head of water recorded in column (2).

Column (5) gives the differences between the numbers in columns (3) and (4).

Column (6) gives the difference in temperature calculated from the constants of a theoretical equation to be developed later.

Table IV.—Results for Water.

(1) Water condensed in 10 minutes.	(2) Height of water above orifice.	(3) Observed rise in temperature.	(4) Rise calculated from half-height assumption.	(5) Differences.	(6) Rise calculated from theory.
c.c.	cm.	° C.	° C.		° C.
8	3 ·95	0 ·0272	0 ·0510	0 ·0338	0 ·0253
8	4 ·8	0 ·0340	0 ·0620	0 ·0280	0 ·0338
8	4 ·9	0 ·0353	0 ·0634	0 ·0281	0 ·0348
8	4 ·9	0 ·0348	0 ·0634	0 ·0286	0 ·0348
8	5 ·0	0 ·0363	0 ·0647	0 ·0284	0 ·0358
8*	5 ·65	0 ·0410	0 ·0731	0 ·0321	0 ·0427
8	6 ·0	0 ·0465	0 ·0776	0 ·0311	0 ·0465
8	6 ·1	0 ·0484	0 ·0789	0 ·0305	0 ·0476
8*	6 ·8	0 ·0517	0 ·0880	0 ·0363	0 ·0554
8	7 ·6	0 ·0627	0·0983	0 ·0356	0 ·0645
16	3 ·85	0 ·0220	0 ·0498	0 ·0278	0 ·0213
16	4 ·8	0 ·0299	0 ·0620	0 ·0321	0 ·0300
16	4 ·85	0 ·0309	0 ·0627	0 ·0318	0 ·0305
16	4 ·95	0 ·0315	0 ·0640	0 ·0325	0 ·0314
16	5 ·2	0 ·0344	0 ·0673	0 ·0329	0 ·0339
16	5 ·2	0 ·0342	0 ·0673	0 ·0321	0 ·0339
16	5 ·6	0 ·0362	0 ·0724	0 ·0362	0 ·0378
16	6 ·6	0 ·0481	0 ·0854	0 ·0373	0 ·0481
32	4 ·8	0 ·0234	0 ·0620	0 ·0386	0 ·0236
32	5 ·4	0 ·0270	0 ·0698	0 ·0428	0 ·0285
32	7 ·5	0 ·0500	0 ·0970	0 ·0470	0 ·0475

* There was some uncertainty in the rate of passage of steam in these experiments.

It is at once apparent that the numbers in column (4) fail to represent the facts. And on comparing results for the same height of liquid, but different rates of passage of steam, it is evident that the faster the steam passes the less the rise of temperature. This latter effect is well shown in Table V.

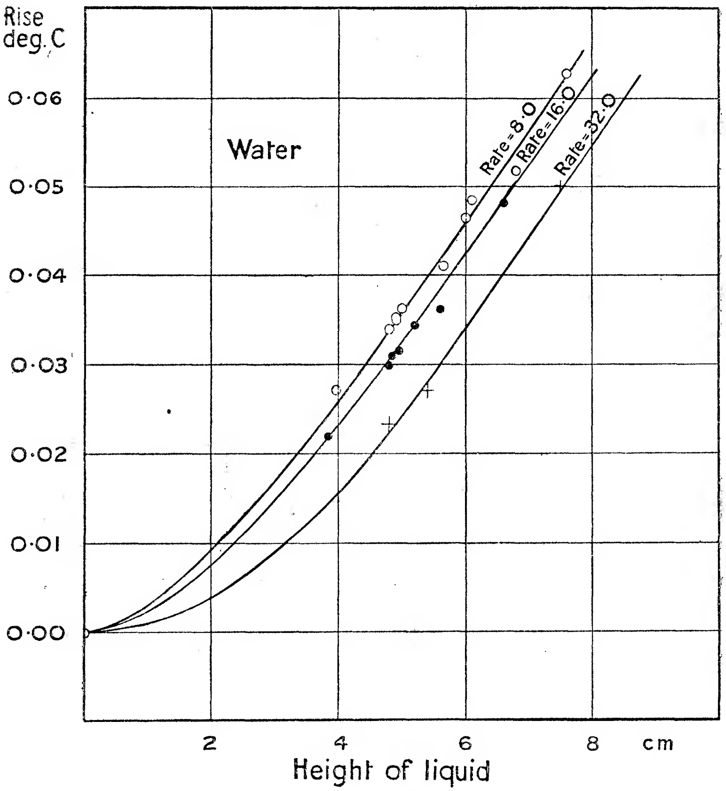
The height of liquid above the orifice in these experiments was in most cases 5 cm., but some of the numbers are intrapolated to that height from the graphs of rise of temperature with height.

The results tabulated in Table IV are plotted in curve (1). It will be seen that the points do not lie on a straight line, but on a curve convex to the axis along which the height of the liquid is measured, but the curves approximate to straight lines as the height of liquid increases.

Table V.—Effect of varying the Rate of Steam.

Rate.	Rise in temperature.
	° C.
1·2 c.c. water condensed in 10 mins.	0·0481
6·6 ,, ,, ,, ...	0·0370
8·7 ,, ,, ,, ...	0·0356
9·35 ,, ,, ,, ...	0·0347
14·1 ,, ,, ,, ...	0·0325
15·7 ,, ,, ,, ...	0·0319
15·7 ,, ,, ,, ...	0·0316
16·0 ,, ,, ,, ...	0·0326
18·3 ,, ,, ,, ...	0·0321
32·8 ,, ,, ,, ...	0·0225
32·8 ,, ,, ,, ...	0·0243

Curve 1.



From the nature of the phenomena it is evident that the curve must (in the case of water) pass through the origin, and this point is the temperature of the steam in the hypsometer.

On drawing the curve it is found that the points lie on a hyperbola, and this hyperbola cuts the axis of temperatures approximately at right angles.

THEORY.

Effect of Varying the Height of Liquid (*the Rate of Bubbling remaining Constant*).—(1) In the following theoretical discussion, we will measure all temperatures, vapour-pressures, and steam pressures (by steam pressures we mean the pressure of the steam in the bubbles or in the free space above the liquid) from the hypsometer point, that is, from the temperature and pressure of the steam in the hypsometer at the moment of observation.* In so far as the temperatures are concerned, the differential arrangement of the platinum thermometers accomplishes this automatically.

Incidentally it may be mentioned that the reasoning is applicable to the equilibrium temperatures of any boiling solution, even when saturated.

(2) The notation used is:—

p = the vapour-pressure of the liquid when in temperature equilibrium.
t = the corresponding temperature.
P = the pressure of the entering steam; obviously this pressure is that due to the total height h of liquid.
T = the temperature corresponding to P, that is, the temperature of boiling water when its vapour-pressure is in equilibrium with steam under the pressure of the atmosphere together with that due to the height h.
P_1 = the mean pressure of the steam in the bubbles during their traverse through the liquid.
T_1 = the mean temperature of the bubbles.

(3) To simplify the argument we will make the following assumptions, which will be dealt with later:—

(*a*) The change in the vapour-pressure of a liquid with change in the hydrostatic pressure upon the latter may be neglected.

(*b*) The hydrostatic adjustment of pressure in the bubbles is practically instantaneous; but, as can be seen by the fact that the bubbles remain in existence at all, the vapour adjustment across the interface only takes place in a time longer than is required for a bubble to traverse the liquid.

---

* Sakurai ('Chem. Soc. Journ.,' 1892, vol. 61, p. 495) showed that unless special precautions were taken to avoid wetting the thermometer or walls of the vessel in the space above the surface of the liquid, the free steam in that space was always at the hypsometer point.

(*c*) The bubbles on entering the liquid are all of the same size (see later).

(*d*) The height of the liquid has no appreciable effect on the size of the bubbles as they ascend (see later).

(*e*) The main cause of the adjustment of temperature is the heat of condensation (or evaporation) of steam at the bubble interface and at the free surface. There is, however, a small radiation effect which will be dealt with later.

(4) Consider now the actual apparatus; it is easy to see that if there were no stirring the liquid would be hotter at the bottom than at the top, and would have corresponding vapour-pressures at these levels. Efficient stirring causes the whole mass to take up a temperature and vapour-pressure somewhere intermediate between these extremes, so that the pressure of the entering steam is higher than the vapour-pressure of the liquid, while at the surface the vapour-pressure is higher than the hypsometer steam pressure.*

(5) In the experiments we establish a temperature equilibrium—hence the rate of cooling must equal the rate of heating.

From the construction of the apparatus cooling practically only takes place at the free surface (in the case of solutions, the loss of heat through the walls of the boiling vessel may be appreciable—we discuss this point in the succeeding paper). The rate of cooling will be approximately proportional to the small difference between the vapour-pressure of the liquid and the hypsometer pressure, that is, proportional to p; as this takes place across the free surface, whose area is independent of the height of liquid, we may put the rate of cooling $= bp$, where b is a constant depending on the free surface area.

(6) In a similar manner the rate of heating is proportional to the pressure difference between the mean steam pressure in the rising bubbles and the vapour-pressure of the liquid, that is to $\mathrm{P}_1 - p$; it is also proportional to the number of bubbles in the liquid, that is to h. The rate of heating may therefore be put $= ah\,(\mathrm{P}_1 - p)$, where a is dependent on the mean bubble area, which, by hypothesis, is constant for the same rate of bubbling, and is independent of the height of liquid.

(7) Equating the rates to one another, we get

$$bp = ah\,(\mathrm{P}_1 - p). \tag{1}$$

---

* If there were no heat losses the stirred liquid would have a vapour-pressure and temperature exactly midway between the extremes; that is, its vapour-pressure would be $h/2$, while the temperature would be the boiling point of the liquid when under the same pressure. Thus the bubble in the first half of its rise would impart heat to, and in the second half it would receive heat from, the liquid.

Remembering that $P_1 = k_2h$, that $p = k_1t$, and putting $\beta = b/a$, the equation reduces to

$$t = kah^2/(h+\beta), \tag{2}$$

where k is a new constant.

The form of curve represented by this equation is a hyperbola cutting the axis of temperatures at right angles, at the point where $t = 0$, that is, at the temperature of the steam in the hypsometer.

As a test of this formulation, we have included in Table IV, in column (6), the equilibrium temperatures for different depths of water calculated by means of equation (2) from the respective hypsometer point and one other point on the graph of height against observed rise. On comparing columns (3) and (6), it will be seen that there is a satisfactory agreement between the numbers.

The constants used in the calculation were—

$k = 0{\cdot}0131$, and
$\beta = 4{\cdot}14$ for a rate of condensation of steam of 8 c.c. in 10 mins.
$\beta = 5{\cdot}26$ „ „ „ 16 „
$\beta = 8{\cdot}0$ „ „ „ 32 „

Dealing with the assumptions (*c*) and (*d*) together, the following would seem to justify them. In the drop method of determining surface tension, it is proved that the size of the drop is, for the same orifice, solely a function of the surface tension and the density; similarly, if we neglect the effect of the momentum of the stirred liquid (this is allowable, as it is practically independent of h), the size of the bubble as it leaves the orifice is a function of the surface tension between water and steam, and also of the difference in density between the contents of the bubble and the water it displaces. As neither of these factors vary appreciably, the bubbles may be taken to be, initially, of the same size.

There are, however, three effects to be considered: (1) It is obvious that the bubble expands as it rises through the liquid. Calling its initial volume m_0, its final volume (m) on emerging will be $m = m_0(H+h)/H$ (where H is the barometic height), its mean volume $\overline{m}$ will be $\overline{m} = m_0(1+h/2H)$, and the mean area $\overline{\Sigma}$ will be $\overline{\Sigma} = \Sigma_0(1+h/3H)$. This change in area is negligible.

(2) Although, initially, the bubbles are of the same size, a difference in the height of liquid produces a difference in the pressure of the steam they contain. Using the same symbols, with the suffixes 1 and 2 to refer to different heights h_1 and h_2, it is easy to see that the ratio of the mean areas will be $\overline{\Sigma}_1/\overline{\Sigma}_2 \doteqdot (1+(h_1-h_2)/3H)$. This also is negligible.

(3) The amount of steam condensed in the liquid is so small (maximum

rate of rise of height equals 1 mm. in one hour) that the consequent change in "bubble" area may also be neglected.

Dealing now with the radiation mentioned in paragraph (*e*); the following seems to fix an upper approximate limit to the effect. On account of the high opacity of water and aqueous solutions to low heat rays, we may assume that the radiation from the liquid is chiefly a surface phenomenon, but with steam, which is more transparent, it will be a volume effect.

There are two radiation interchanges to be considered: (1) the cooling across the free surface of the liquid—the rate at which this cooling takes place is independent of the height, and depends only on t, the effect being small* we may take the rate as proportional to t, and put it equal to bk_0t; (2) the second radiation interchange, which is that between the liquid and the bubbles, is, in the case of water, a heating effect, but in the case of most saturated solutions, where the liquid is hotter than the entering steam, there is a loss of heat; in either case the same function applies. There is little doubt that the bubbles, for the most part, attain a temperature equilibrium with the liquid before they leave it; otherwise when the thermometer is moved about there would be fluctuations in the galvanometer; assuming this,† then, as before, the rate is proportional to the differences between the temperature of the liquid and that of the entering steam T, and we may put it $= \pm v(\mathrm{T}-t)$, where v is a constant depending upon the volume of the bubbles.

Adding these two corrections to equation (1), and remembering that T is proportional to h, it reduces to

$$t = (\mathrm{A}h^2 \pm \mathrm{C}h)/(h+\mathrm{D}). \tag{3}$$

The constants are altered so as to simplify the equation.

This equation represents a hyperbola, but it no longer cuts the axis of temperatures at right angles. In the next paper, where we deal with the much greater radiation losses in the saturated solutions, the experiments show that even there these losses may be neglected; we may therefore take it that equation (2) represents the observations.

Anomalies Due to Varying the Rate of Bubbling.—The results of varying the rate of passage of steam are given in Table V and plotted in Curve 2. As already stated, it is apparent that an increase in the rate of steam is accompanied by a fall in temperature.‡

This change is, at first sight, somewhat surprising; it would be thought that the area of the steam bubbles in contact with the water at any moment, and therefore the heating effect, would be approximately proportional to the rate at which the steam was supplied.

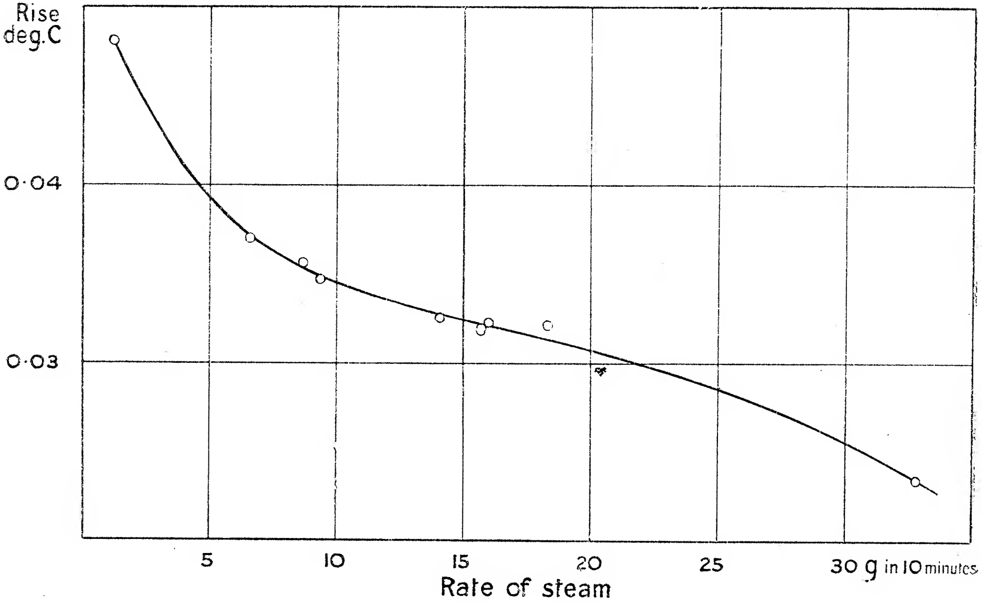
---

* This, even in the case of saturated solutions, when $t = 20°$, is shown in the next paper to be so.

† We are here dealing with an upper limit, for it is easy to show that if we assume that the bubbles do not reach temperature equilibrium before they leave the solution, we shall get exactly the same form of equation as in equation (2).

‡ *Cf.* Sakurai, *loc. cit.*

CURVE 2.



We would offer the following tentative explanation of the apparent paradox:—The area of the steam bubbles in contact with the water at any instant depends not only on the rate at which the steam is supplied, but also on the velocity with which the bubbles pass through the liquid. Now, in the experiments a more or less rapid circulatory motion is always imparted to the water, and, as far as eye observations enabled us to judge, the velocity of circulation was roughly proportional to the rate of supply of steam; consequently, since the whirl of liquid carries the bubbles with it, it follows that their velocity is also proportional to the rate of steam supply, and, further, there was distinct evidence that with the faster rates of bubbling there was a tendency for the bubbles to coalesce, thus reducing the heating surface.

We may take it, therefore, that the factor a in equation (1), instead of increasing with an increase of steam supply, actually diminishes. On the other hand, the rapid passage of bubbles tends to increase the cooling surface by the extension of the free surface on account of agitation, and also by throwing particles of water into the hypsometer space above. Thus the factor b of the equation is increased.

It will be seen on referring to the values of β given on p. 485 that for an increase of passage of steam from 8 to 16 c.c. in 10 minutes, $\beta (= b/a)$ increases about 20 per cent., an increase which does not seem incompatible with the foregoing discussion. The rate of 32 c.c. in 10 minutes was much too fast for any bubbles to be seen. A further test of equation (1) was made by observing the rise in boiling point in a vessel of a larger diameter. The results are tabulated below :—

Table VI.—Comparison of Vessels of different Diameters.

Height of liquid.	Rate of steam.	Observed rise in vessel of diameter 4·4 cm.	Observed rise in vessel of diameter 5·75 cm.
cm.	c.c. in 10′.	° C.	cm.
5·5	9·1	0·0384	0·0309
5·6	9·2	·0393	·0338
6·7	5·2	·0561	·0477
6·8	7·9	·0532	·0455
7·6	11·5	·0591	·0510
7·8	11·5	·0620	·0540

It will be seen that the increase in the evaporation surface causes a considerable fall in temperature in each experiment. The fall in temperature is only 70 per cent. of that calculated on the assumption that we are dealing with a change of free surface proportional to the change in the cross section of the vessels. We think the discrepancy is sufficiently accounted for when it is remembered that the free surface is a turbulent one, and the form of the vessel and the shape of the steam jet will influence this very considerably. In the wide vessel the jet pointed downwards at an angle of about 45°, while in the small apparatus it was approximately horizontal.*

That the form of the jet has considerable influence on the circulation, and consequently on the free surface, was proved by experiments which need not be detailed here. It was found that in the same vessel, and under the same conditions of bubbling and height, a jet pointed vertically downwards raised the temperature higher than one placed horizontally, both jets having the same diameter.

Conclusions.—The constant temperature at which a liquid boils, as distinguished from the "hypsometer" point, is a function of several factors, among which are the height of liquid, the rate of passage of the vapour bubbles, etc. To get comparable results the observed values must be extrapolated down to a hypothetical value for an infinitely small layer of liquid. This temperature will be the "hypsometer" point. As these variable factors are operative in any method of boiling a liquid, heating by a flame or by an electric current will give no better results than the method we used. Here again it is necessary to obtain a series of observations and extrapolate to an infinitely small layer of liquid.

---

* Mr. W. E. S. Turner, 'Journ. Chem. Soc.,' 1910, vol. 97, p. 1184, finds that the rise in the boiling point of chloroform is smaller than that due to a pressure of half the height of the liquid, and that it is smaller the wider the vessel.

In the case of solutions, the hypsometer point cannot be determined directly, so that we must fall back on determinations of the temperatures of the boiling liquid; these are also variable, and it would seem that a definition of what is meant by the boiling point of a solution is required. We would suggest the following:—Assuming that the solution is under a standard atmospheric pressure of 760 mm. of mercury, then the boiling point is the temperature of a small layer when its vapour is in equilibrium with the free vapour above it.

On the Boiling Points of some Saturated Aqueous Solutions.

By The Earl of Berkeley, F.R.S., and M. P. Appleby, M.A., B.Sc. (Oxon).

(Received March 23, 1911.)

Introduction and General Discussion.—These experiments were made so as to obtain as accurate data as we could for the purpose of calculating the osmotic pressures of the solutions. The method for determining the boiling points was that already detailed in an earlier communication to the Society,* except that differential platinum thermometers were used as described in the paper "On the Boiling Point of Water."

One of the platinum thermometers was always in the hypsometer, and to get the true boiling point as defined in our previous paper the height of the barometer and height of solution were systematically noted. The chief difficulty of the experiments was that of keeping the solutions saturated. It was found necessary to use a large quantity of finely powdered salt, and to keep the solid in rapid motion by a sufficiently powerful current of steam. If large crystals are used, or if the salt has been left in contact with the solution too long at the end of an experiment, so that crystals have grown, the next experiment will give low values for the equilibrium temperature, showing that the solution is not saturated. At times it happened that a paste of crystals was formed, which offered so much resistance that the

* Berkeley, 'Phil. Trans.,' A, 1904, vol. 203.